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Rheological Evaluation of Asphalt Cements Modified With ASA Polymer and Al_2O_3 Nanoparticles

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Abstract

This study aims to evaluate and characterize the properties of modified asphalt cements exposed to high temperature. The Acrylate Styrene Acrylonhrtilrei (ASA) polymer and nano aluminum oxide (Al_2O_3) nanoparticles were added to the base asphalt cement with concentrations of 3, 5 and 7% of the weight of asphalt. The storage stability, viscosity, frequency sweep and MSRC test were considered for evaluation. The results demonstrate that the addition of ASA polymer and Al_2O_3 nanoparticles content have a great influence on the rheological properties of the asphalt cement at high temperatures. Additionally, it is clear that the storage stability of modified asphalt cements with ASA polymer and Al_2O_3 nanoparticles has good compatibility among the asphalt cement and the modifiers. Moreover, the complex modulus (G*) improves as the concentration of both modifiers increases. The improvement was 63.70% for 5% ASA polymer, and 71.12% for 5% Al_2O_3 at 75 °C. Moreover, the modified asphalt cements demonstrates great resistance to high temperatures rutting, as the enhancement was up to 80 and 59% for 5% concentration of ASA and Al_2O_3. The modification of asphalt cements provides increasing the creep recovery up to 69.23 and 62.53%. It was found that the usage of ASA polymer and Al_2O_3 nanoparticles is able to mitigate asphalt cement problems at high temperatures, and 5% is considered as the optimum content of both modifiers.

Keywords: ASA polymer, Al_2O_3 nanoparticles, dynamic shear rheometer and multiple stress creep and recovery

1 Introduction

Asphalt is a dark brown to black cementation material in which the predominating constituents are bitumen, which occur in nature, or in petroleum processing. Asphalt is viscous liquid or solid that essentially consists of hydrocarbons and their derivatives, which soluble in carbon disulfide (Lesueur,

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2009). They are substantially nonvolatile at ambient temperature, and gradually soften when exposed to heat. Asphalt has been used for many years, and its importance as a valued engineering material continues to increase.

The binding material has been widely applied in the construction of highways and road networks, since asphalt is able to resist stresses due to traffic loads and temperature (Albrka et al, 2014). Due to the limitation of temperature susceptibility, low, intermediate and high temperatures and temperature performance of asphalt need to be enhanced. Therefore, the modification of base asphalt is necessary to improve the material's performance (Fang et al, 2013; Peters et al, 2010; Yildirim, 2007). There are several types of asphalt modifiers, including rubbers, sulfur, polymers, fibers and nanomaterials (Fang et al, 2013; Yao et al, 2012; Zare-Shahabadi et al. 2010). Recent roads need to show better performance under high traffic density and axle loading than those of the past. The application of modified binders offers a promising method to improve asphalt cement and asphalt mixes (Lu & Isacsson, 2000). It has been observed for a long time that the use of polymer modified asphalt cement (PMAC) achieves better asphalt cement performance, the polymer content and characteristics have a significant role to enhance the properties of PMAC (Fu et al, 2007).

Polymeric additives such as block copolymers, crumb rubber or recycled polymers have been widely used to enhance in-service asphalt properties. Therefore, asphalt additives should be able to improve binder properties at low, intermediate and high service temperatures. Moreover, when was used as modifiers of asphalt, the selected polymers should be compatible with asphalt cement in the blended process with conventional mixing equipment, and can manage to keep up their main properties. The most ordinarily used polymers worldwide include 75% elastomer modified asphalt cement, 15% plastomers and 10% belongs to either crumb rubber or other modifications (Mubaraki, 2015, Mubaraki et al, 2013, Habib et al, 2011). Polymers that have been used as modifiers of asphalt cement can be divided into two categories, namely (i) elastomers such as crumb rubber (CR) and styrene butadiene styrene (SBS), and (ii) plastomers such as polyethylene (PE) and ethylene vinyl acetate (EVA).

Elastomers modifiers of asphalt work to extend the low and high service temperatures of asphalt, whilst plastomers are known as efficient modifiers at high service temperatures (Al-Hadidy & Yi-Qiu, 2009; Ameri et al, 2013; Kök & Çolak, 2011). The main disadvantage of PMAC is the lack of stability during elongated storage at high temperatures. The tendency to phase separation under quiescent conditions is an important limitation for the practical use of these blends (Masson et al, 2003).

Nanotechnology is currently been rapidly incorporated into the field of asphalt cement, with various kinds of nanomaterials being used to modify asphalt cement and asphalt mixes. It was found that nanomaterials are able to enhance the performance of asphalt cement and mixes. A study conducted by You et al. (2011) concluded that nanoclay modified asphalt could reduce the strain failure rate and increase the stiffness (shear complex modulus) of base asphalt. Moreover, the addition of nanoclay would decrease the moisture damage of the asphalt mixes (Yao et al, 2012; You et al, 2011). Moreover, using single-wall nanotube materials to modify the asphalt cement shows that the performance grade of the modified asphalt cements increase, and the elastic element of the complex modulus of the base asphalt was less than the modified asphalt cements (Shiman et al, 2011). Based on the study presented by Yao et al. (2012) using nanosilica to modify asphalt, they found that the addition of nanosilica slightly decreases the viscosity rates of base asphalt cement. Lower and higher viscosity values of asphalt have an influential role to determine the mixing and compaction temperatures. Moreover, the addition of nanosilica is able to reduce and delay the aging process. The modification of asphalt cement using polymers and nanomaterials can improve overall the performance, durability and physical properties of asphalt cement.

2 Experimental Design

2.1 Materials

Base asphalt cement 60/70 penetration grade was obtained from a factory at Port Klang, Malaysia, while the Acrylate Styrene Acrylonhrtilrei (ASA) polymer and the nano aluminum oxide (Al_2O_3) were supplied from Shijiazhuang Chanchiang Corporation Company in China. The physical properties of the base asphalt cement and the ASA polymer are shown in Table 1.

Material	Properties	Test Method	Value
Bitumen 60/70	Specific Gravity	ASTM D70	1.03
	Penetration @ 25 ˚C	ASTM D5	70
	Softening point (˚C)	ASTM D36	46.0
	Viscosity @ 135 ˚C (Pa.s)	ASTM D4402	0.5
	Ductility (cm) @ 25 ˚C,	ASTM D113	≥125
ASA	Specific Gravity	-	0.30
	Size mm	-	2
Nano Al_2O_3	Size nm	-	13

Table 1: The Physical Properties of the Base Asphalt Cement, ASA and Al_2O_3

2.2 Sample Preparation

The modified samples in this study were prepared using the melt blending method by adding 3, 5 and 7 % content by weight of both modifiers (ASA polymer and Al_2O_3 nanomaterials) to asphalt cement. The asphalt was heated until it was transformed into fluid from, and a Silverson high shear mixer was used for the mixing process at 170˚C (±1 ˚C) under a speed 5000 rpm for one and a half hours to produce homogenous mixtures.

2.3 Viscosity Test

A Brookfield rotational viscometer in this study was used to determine the viscosity of the base and modified asphalt cements samples. Spindle No. 27 was used at a rotational speed of 20 rpm according to Superpave test parameters (Asphalt Institute 2007). Three readings were noted for each test temperature, and the average value was accepted as the final test result. The test performed under temperatures of 135°C and 165°C for all samples.

2.4 Storage Stability Test

The base asphalt cement and modified asphalt cements storage stability was measured as follows. The samples were poured into an aluminum foil tube with a height of 16 cm and diameter of 3 cm. The foil tubes were closed and stored vertically at a temperature of 163 ± 5°C in an oven for 48 hours. They were then cooled at room temperature and divided horizontally into three equal parts. The samples extracted from the top and bottom sections were used to assess the storage stability of the ASA polymer and Al_2O_3 nanomaterials modified asphalt cements by determining the sections softening points. If the difference between the top and the bottom parts was less than 2.5 °C, the samples were considered to have good high temperature storage stability. If the softening points differed by more than 2.5 °C, the samples of the modified asphalt cements were considered to be unstable (Zhang et al, 2011).

2.5 Rheological Properties

The dynamic shear rheometer (DSR) is used to test asphalt cement and measure its rheological properties, including complex shear modulus (G*) and phase angle (δ) at test temperatures that range from intermediate to high. These parameters can be used to characterize both viscous and elastic behaviors of asphalt cement. The values of G* and (δ) for asphalt cements are highly dependent on the test temperature and frequency of loading. In this study, the Rheometer HAAKE Rheo Stress 600 from the Thermo Electron Corporation was used to investigate the high temperatures rheological properties of base and modified asphalt cements using a frequency sweep test and multiple stress creep recovery (MSCR). The applied frequency sweeps were in the range of 1 to 100 rad/s (0.159 -15 Hz), and the temperature was kept consistent at 75 ˚C. Regarding the MSCR two different stress levels were used 100 Pa and 3200 Pa, and the test was performed at temperature of 65 ˚C. Moreover, 25 mm diameter spindle with a gap of 1 mm was used in both DSR tests.

3 Results And Discussion

3.1 High Temperature Viscosity

The impact of addition of concentration and temperature on the viscosity of ASA polymer and Al_2O_3 nanoparticles modified asphalt cements is shown in Figure 1. As can be seen, the viscosity of the modified asphalt cements, regardless of the concentration, decreases with increasing the temperature, this similar trend was also observed in base asphalt cement. The increment of ASA polymer and Al_2O_3 nanoparticles concentration can significantly increase the asphalt cement viscosity, which means increased the asphalt thickness and better coating of aggregates in the asphalt mixture. In addition, the modified asphalt with Al_2O_3 nanoparticles has a value of viscosity that is higher than modified asphalt cements with ASA polymer.

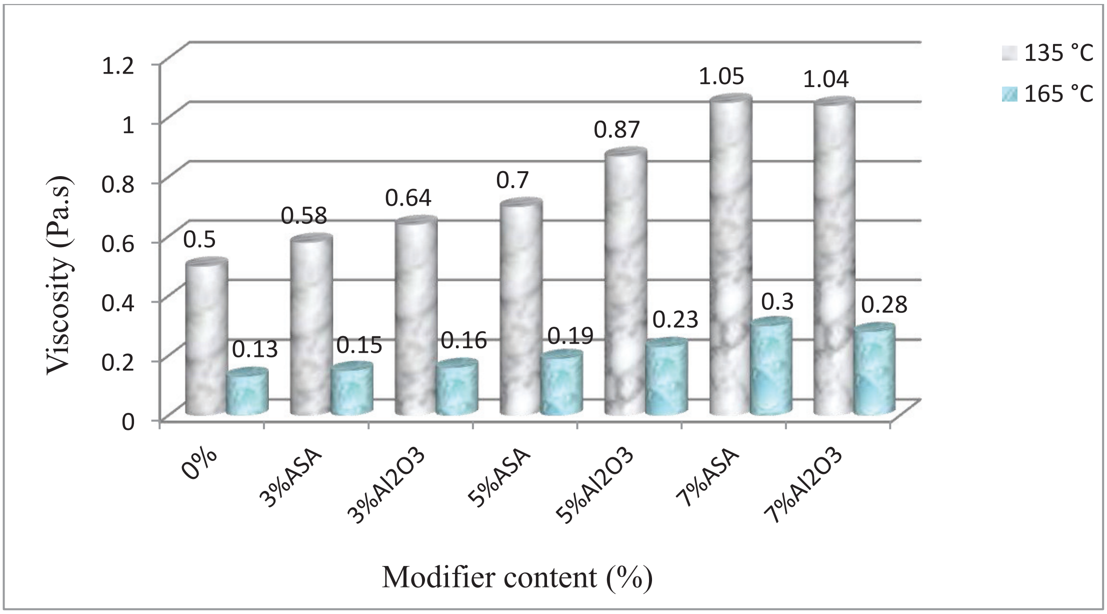


Figure 1: Viscosity of Base, ASA Polymer and Al_2O_3 Nanoparticles Modified Asphalt Cements

3.2 High Temperature Storage Stability

According to the difference in the density between asphalt cement and ASA polymer, phase separation can occur in the ASA polymer modified asphalt cement during storage at high temperatures. Meanwhile, the small size of the nanoparticles gives it the ability to have great workability and compatibility. However, an agglomeration might take place in Al_2O_3 nanoparticles modified asphalt cements. The storage stability samples of the base asphalt cement, ASA polymer and Al_2O_3 nanoparticles modified asphalt cement results are shown in Figure 2. It can be observed from Figure 3 that the difference in the softening points among the base asphalt cement and the modifiers was up to 12 °C. Moreover, the enhancement of the softening point of modified asphalt cements means the asphalts are becoming harder than the base asphalt cement. In addition, the differences between the top and bottom of the ASA polymer modified asphalt cements are less than 2.5 °C for 3 and 5% ASA, which means the ASA polymer was stable during stored at high temperatures. Meanwhile, for 7% ASA the differences exceed the permitted value, which means phase segregation between the base asphalt cement and the ASA polymer increase when increasing the concentration of the polymer.

The modification of asphalt cement using Al_2O_3 nanoparticles shows that all modified asphalt samples have great storage stability at high temperatures as the differences between the top and bottom sections are less than 2.5 °C. It is observed that even though 7% Al_2O_3 still stable, the differences in the top and bottom sections increased compared with 5% Al_2O_3, which means agglomeration takes a place among the nanoparticles with increase their in asphalt cement. In general, the modified asphalt cements with Al_2O_3 nanoparticles has great storage stability compared to the samples modified with ASA polymer.

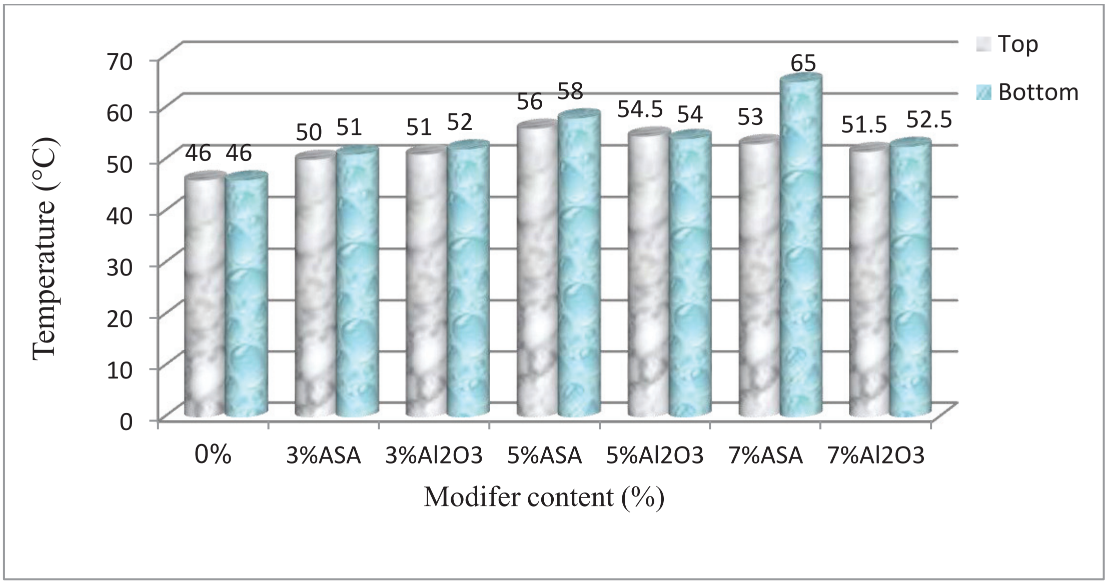


Figure 2: Storage Stability of Base Asphalt Cement, ASA Polymer and Al_2O_3 Nanoparticles Modified Asphalt Cements

3.3 High Temperature Rheological Properties

This section discusses the results obtained from the DSR tests, including frequency sweep test and multiple stress creep and recovery (MSCR) test.

3.3.1. Isochronal Plot

A plot of some viscoelastic variable, such as the complex modulus or phase angle versus temperature at a constant frequency or loading time is knows as an isochronal plot. Thus, viscoelastic data can be presented over a range of temperatures at a given frequency using an isochronal plot. Therefore, the isochronal plots of the complex modulus G* versus temperature (°C) at the frequency of 1 rad/s (0.159 Hz) are shown in Figure 3. It shows that the increase in the G* value of modified asphalt cements similar to increase in viscosity. Increased G* values were consistently observed for all modified asphalt cements compared to the base asphalt cement, and the best performance of modified asphalt was with the addition of 5%ASA sample for polymer and 5%Al_2O_3 nanoparticles. The highest value of G* is more resistant to the rutting parameter, and for 7% concentration of ASA polymer and Al_2O_3 nanoparticles modified asphalt cement shows a slight decrease in G* value as a result of phase segregation and agglomeration respectively.

3.3.2. Effects of Temperature on Rutting Factor

In the Superpave method, the G*/sin δ value is the parameter used to evaluate the permanent deformation (rutting) of the asphalt cement. The specifications of Superpave identify a minimum value of 1.0 KPa for the G*/sin δ of base asphalt cement at performance grade temperature. Figure 4 shows the rutting parameter of base asphalt cement, ASA polymer and Al_2O_3 modified asphalt cements. It can be realized that the addition of both modifiers has the ability to greatly increase the resistance of asphalt to the permanent deformation. Base asphalt cement has the lowest value of G*/sin δ, while 5%Al_2O_3 has the highest value of G*/sin δ amongst all the tested samples. It is observed that as the concentration of both modifiers increase, the resistance of asphalt cement to rutting parameter increased up to 5%. Different behavior is shown at 7% as the value of G*/sin δ reduced slightly as the compatibility of polymer modified asphalt cements decline as a results of phase segregation and agglomeration which occur softness in modified asphalt cements.

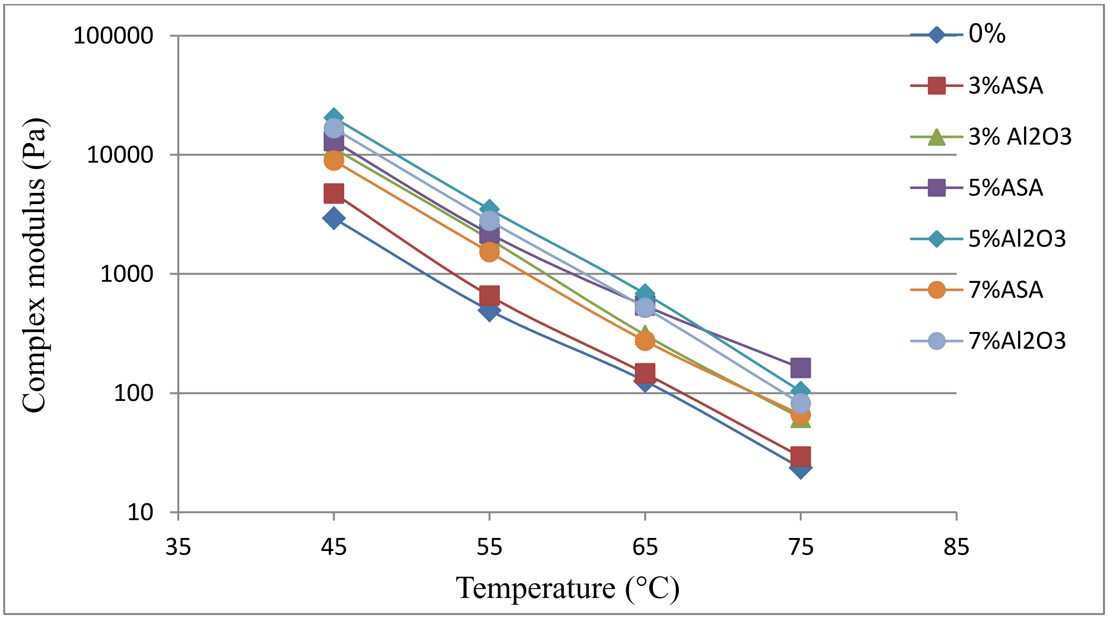


Figure 3: Isochronal Plots of G* of Base Asphalt Cement, ASA Polymer and Al_2O_3 Modified Asphalt Cements

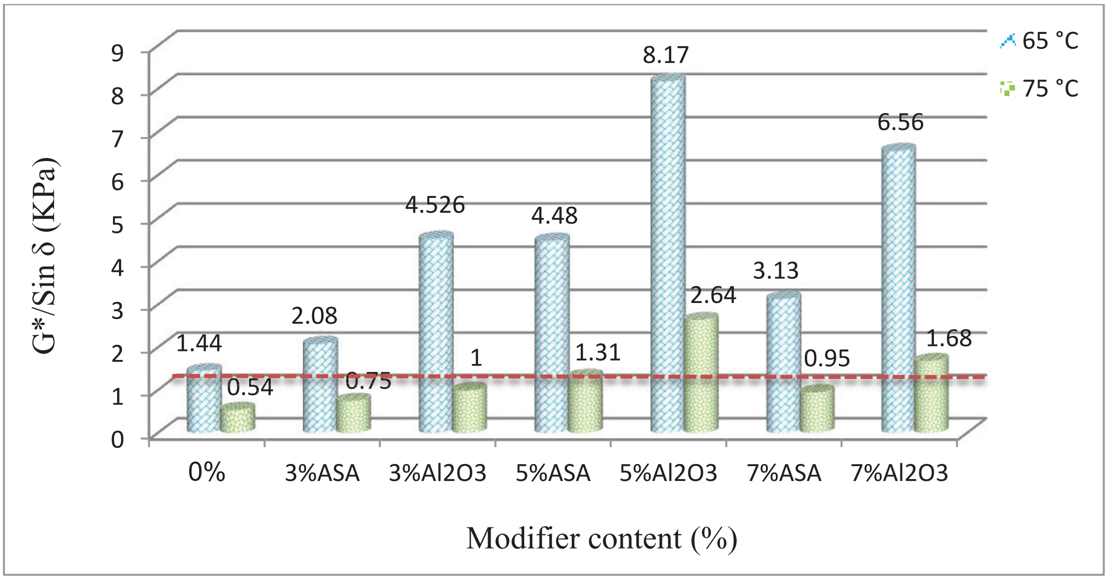
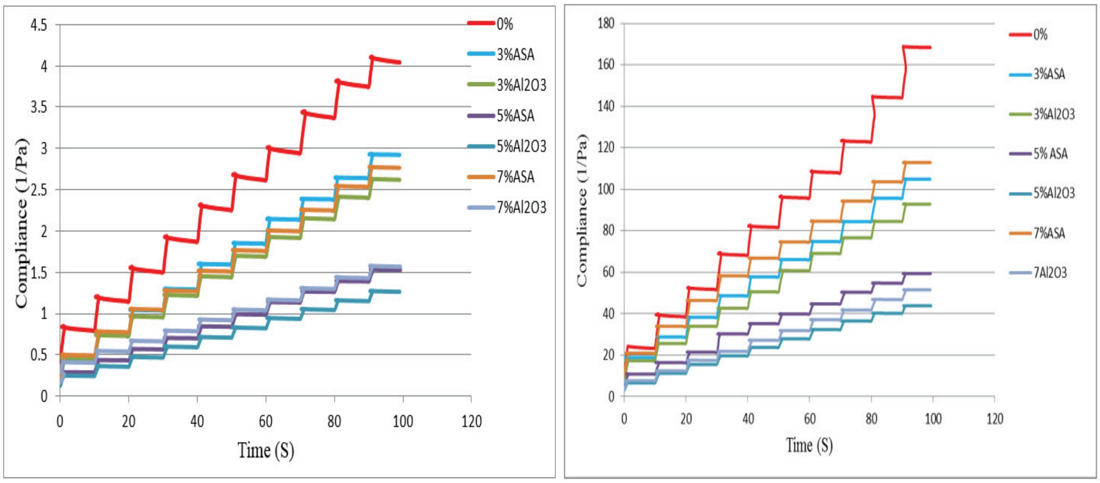


Figure 4: Ratting Parameter of Base Asphalt Cement, ASA Polymer and Al_2O_3 Modified Asphalt Cements

3.3.3. MSCR Test

Accumulated creep compliance is the output of MSCR tests of the base asphalt and modified asphalt cements. The ratio of strain to the applied stress is defined as Compliance. Figure 5 shows all cycles of accumulated creep compliance at each stress level. It can be realized that the accumulated creep compliance (Jacc) at low stress level (100 Pa) is low, and it increases once the stress level is increased (3200 Pa).



(a) (b)

Figure 5: MSCR at 64 °C for Base and Modified Asphalt Cements at 100 (a) and 3200 Pa (b)

Moreover, the results indicate that the ASA polymer and Al_2O_3 nanoparticles have great influences on the asphalt cement behavior. All types of modified asphalt cements have a greater value compared with base asphalt cement, and 5% Al_2O_3 has the best creep recovery, which means better resistance to permanent deformation among the modified asphalt cements, regardless of the stress levels. However, the Al_2O_3 nanoparticles show a high level of improvement in creep recovery compared with ASA polymer, which has a good effect on the rheological properties of base asphalt cement. The percentages of the recovery were 34.6% for 3% Al_2O_3; 69.23% for 5%Al_2O_3; and 61.8% for 7%Al_2O_3. Meanwhile these values were 27.8% for 3% ASA; 62.63% for 5% ASA; and 31.85% for 7% ASA. This high impact of nanoparticles might be because nanoparticles hardness works to strengthen of base asphalt cement.

4 Conclusions

The study was conducted to evaluate the properties of asphalt cement modified with ASA polymer and Al_2O_3 nanoparticles at high temperatures using a viscosity test, storage stability test, frequency sweep test and MSRC test. The following conclusions can be drawn base on the obtained results:

- The viscosity values of modified asphalt cements increase with an increase in the modifier concentration, and all viscosity values were within the range of the specifications.
- The modified asphalt cements can be stored at high temperatures, especially the modified asphalt cement with Al_2O_3 nanoparticles. Meanwhile, ASA polymer is able to store up to 5% ASA.
- G^* and $G^*/\sin\delta$ values of base asphalt cement were the lowest compared with modified asphalt cements. Meanwhile the 5% Al_2O_3 has the highest value among the modified asphalt cements which means better performance of modified asphalt cement regarding resistance to rutting.
- The results of the MSRC test demonstrate a great creep recovery of modified asphalt cements compared with base asphalt cement. The results indicate that hardness of modified asphalt cements was increased. Besides, it was found that modified asphalt cements were strongly influenced by modifiers from 3% up to 5%, and the improvement reduced for 7%, but is still better than the base asphalt cement.
- In general, the modification of asphalt cement using ASA polymer and Al_2O_3 nanoparticles has a remarkable impacts on the properties of asphalt cement. Furthermore, the modified samples with Al_2O_3 nanoparticles show better results than the samples with ASA polymer, and 5% can be considered the optimum content of both modifiers.

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